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Research article

Adsorption studies of a multi-metal system within acetate media, with a view to sustainable phosphate recovery from sewage sludge

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ABSTRACT

Phosphate shortages and the ensuing pressures on food security have led to an interest in processed sewage sludge as a substitute for commercial fertilisers. The presence of heavy metals in this nutrient source causes concerns around environmental release and pollution. This work builds towards a resin-in-pulp sludge detoxification process. It showcases the kinetic and thermodynamic adsorption capabilities of the ion-exchange resins C107E (carboxylic acid functionality), MTS9301 (iminodiacetic acid) and TP214 (thiourea), with respect to Cu (II), Fe(II), Pb(II) and Zn(II), within a simulated sewage sludge weak acid (acetate) leachate. The isotherms produced in this complex system were quite different to those generated when single metals were investigated in isolation, with desorption of lower affinity species clearly observed at higher equilibrium concentration values. Mixed-metal isotherm data were fitted to common two-parameter isotherm models and also a novel modified Langmuir model, which better accounted for the effects of desorption and competition. Kinetic data were also fit to common two-parameter models; results suggesting the system was likely film diffusion-controlled and followed pseudo-2nd-order kinetics. C107E displayed rapid adsorption of lead ($t_{1/2} = 26 \pm 3$ min), and significant uptake of all metals. MTS9301 showed high affinity for copper ions, with concurrent desorption of all the other metals, and also displayed the fastest kinetics ($t_{1/2} = 14.1 \pm 0.9, 130 \pm 20, 25 \pm 5$ and 49 ± 6 min for copper, iron(II), lead and zinc, respectively). C107E and MTS9301 showed far slower adsorption for iron(II) than the other three metals, which invited the possibility of kinetic separations. TP214 had reasonable effectiveness in removal of copper, but poor affinity for all other metals. The greatest difficulty in modelling the multi-metal system was the two-stage trends observed in equilibrium experiments, as metal-proton exchanges become metal-metal exchanges. While not having the highest capacity, MTS9301 was recommended as the most appropriate resin for rapid and efficient removal of Cu, Pb and Zn from the acetate medium.

1. Introduction

Global supplies of phosphate are experiencing rapid depletion, with great uncertainty over the timescale for full exhaustion of reserves, with predictions varying between 50 and 200 years (Walan et al., 2014). The increasing world population, predicted to reach 10.4 billion by 2050 (United Nations, 2019), acutely raises the issue of food security, as phosphate is an essential ingredient in fertiliser production. There are

significant efforts underway to implement recycling programmes at wastewater treatment plants and reduce overuse in agriculture. Some of these technologies are in full-scale operation, such as the Belgian NuReSys (Nutrient Recovery Systems) process, which precipitates the phosphate out of wastewater as struvite (Desmidt et al., 2015). All processes have inherent drawbacks including low percentage recovery, bioavailability of the final precipitate, economics and preventative legislation (Jupp et al., 2021). Globally, the bulk provision of phosphate

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remains the unsustainable mining of phosphate rock (Walan et al., 2014; Jupp et al., 2021; El Wali et al., 2021).

Phosphate is therefore a seminal challenge in the field of resource recovery and improved technologies are urgently required; both to progress towards a circular economy and to combat the issue of soil impoverishment. Municipal wastewater treatment generates large amounts of solids, rich in phosphate and further plant nutrients (Spangberg et al., 2014). The sludge can be incinerated (Fytli and Zabaniotou, 2008), further concentrating this potential phosphate reserve. While incineration nullifies the pathogenic threat, it also increases the concentrations of heavy metals in the ash (Robinson et al., 2004).

The multitude of wastestreams treated by a municipal waste water plant means that multiple toxic heavy metals, commonly copper, lead and zinc, pass through the processing stages (Robinson et al., 2004; Inglezakis et al., 2014). These metals are often immobilised in the ensuing sludge and the wastestream is thus considered appropriate for use on crops (Smith, 1996). However, the metals may mobilise in oxidative (atmospheric) conditions, leading to contamination of the crop itself, the geosphere and the hydrosphere (Schippers, 2004; Habashi, 1995). Regardless of immobilisation, from a United Kingdom agriculture perspective, the metal accumulation in soils is liable to surpass recommended threshold levels in 70–80 years (Smith, 1996). The presence of heavy metals (as well as pharmaceuticals and pathogens) has resulted in some European countries restricting, and indeed banning, the application of sewage sludge to agricultural land (Jupp et al., 2021).

The metals within sewage, therefore, pose both a great challenge and great opportunity: they are a barrier to more widespread usage of sewage sludge as a fertiliser, but also, in the production of a sustainable phosphate source, could generate a secondary income through hydro-metallurgical recovery of valuable species (Vriens et al., 2017; West-erhoff et al., 2015). Furthermore, in a circular economy, it is important to reuse every component of sewage sludge. Extensive research has taken place into the leaching of heavy metals from a sewage sludge matrix (Fytianos et al., 1998; Gaber et al., 2011; Dacera and Babel, 2006; Azhdarpoor et al., 2015; Marchioretto, 2003; Gu et al., 2017). Such work relies on solid-liquid separation after leaching (Marchioretto, 2003; Gu et al., 2017). Because such separations generate high-moisture solids (Metcalf et al., 1991), mobilised metals commonly partition into the solid waste and complete sequestration of metals is difficult.

Our research group proposes a weak acid leaching system, working in tandem with ion-exchange in a resin-in-pulp (RIP) system (Fig. 1) for remediation of this wastestream and pathway towards valorisation of the contained metals (Bezzina et al., 2019). The leaching stage mobilises

intransigent metallic species. The neutralisation step adjusts the pH to one more favourable to ion-exchange. Finally the contact stage adsorbs mobilised metallic species onto the resin beads, before removal by sieving and separation of the metals in hydrodynamic downstream processes. We are gaining understanding of the various adsorption phenomena that can impact on a chemical separation process by studying the uptake of copper, iron, lead and zinc in a simplified system, where the dominant factor is expected to be the complexing properties of the acetate ion (Martell et al., 1997), present in high concentrations. Copper, lead and zinc were chosen as subjects of study, as they are all problematic heavy metals, generally present in sewage sludge at concentrations of hundreds to thousands of mg kg^{-1} (on a dry mass basis) (Scancar et al., 2000; Tytla, 2019). All have significant toxicity and various studies have demonstrated success in the use of acetic acid as a lixiviant for their leaching from sewage sludge (Gaber et al., 2011; Perez-Cid et al., 2002). In the EU, the respective average concentrations of copper, lead and zinc in sewage sludge are 337, 124 and 1222 mg kg^{-1} , while in the US, these averages are 850, 500 and 1740 mg kg^{-1} (Inglezakis et al., 2014). There are both national and international limits placed on the concentrations of these species in both soils and fertiliser slurries (European Union, 1986). While the averages quoted are an order of magnitude below these thresholds, it must be repeated that successive applications of sludge lead to accumulation of the metal species in soils (Smith, 1996). In contrast, there are no such limitations placed on iron concentration; however, its concentration in sewage is generally one-two orders of magnitude above the more toxic metals (Scancar et al., 2000) and it is therefore a problematic species in terms of competing with the more toxic metals for binding sites on a given adsorbent.

RIP technology circumvents ‘preg-robbing’, which is the unfavourable re-adsorption of the mobilised species of interest from a leachate by a solid-phase component) (Mubarak and Irianto, 2016; Kotze et al., 2005). In this instance, it would act to remove mobile metals from the leach slurry in advance of filtration, thus enabling removal of the resin from the sludge by sieving. Leaching of metals often necessitates low pH, which can compromise the performance of the resin. However, if the lixiviant is a weak acid, with complexing capabilities, as with the acetic acid used in this study, the metals may be stabilised at lower acidity, thus affording a neutralisation stage in the process and increasing metal extraction (Bezzina et al., 2018). Since the RIP system is a static, rather than hydrodynamic uptake process, understanding the underlying chemistry and impact on both equilibrium and kinetic selectivity, in a multi-metal system and batch resin kinetics is fundamental to the engineering design.

Exploration of complicated multi-metal isotherms are rare within

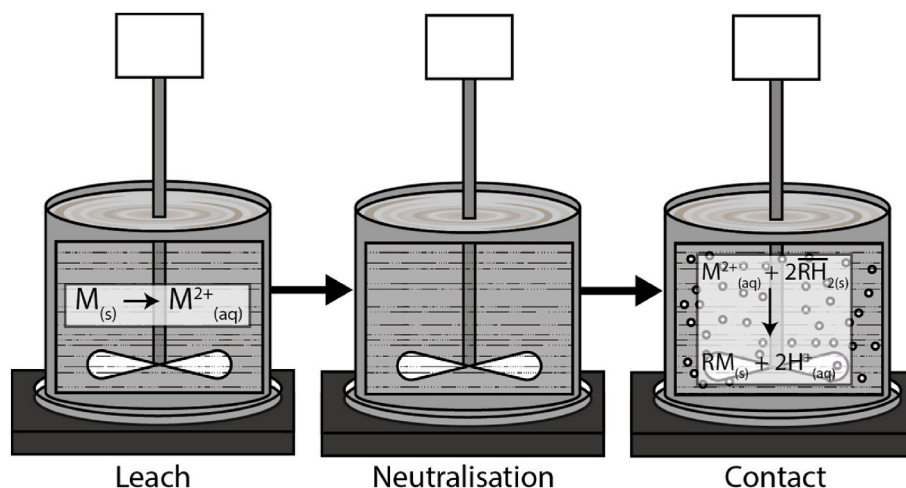


Fig. 1. Hypothesised RIP system for the leaching and adsorption of heavy metals from sewage sludge.

literature and minimal information is available on the effect of saturation on resin capacity for certain metals or competitive desorption. These are issues that will be observed within a complicated leachate system of multiple dissolved metallic species. The kinetic behaviour of a batch system can be dependent on diffusion gradients (both inter- and intra-particulate) (Harland, 1994). Thus extraction may be hindered within the high-solids RIP matrix, again underlying the need to investigate these phenomena.

Previous efforts (Bezzina et al., 2019, 2020) have identified three candidate resins for use within this system, against the criteria of capacity, affinity with the metals and selectivity; albeit in much simplified uptake conditions. These are Purolite C107E (carboxylic acid functionality), Purolite MTS9301 (iminodiacetic acid) and Lanxess TP214 (thiourea). To progress this technology, an understanding of multi-metal adsorption behaviour in terms of kinetics and adsorption-desorption processes is both novel and necessary in order to predict potential performance within a RIP system. This study hopes to produce a step-change advance in understanding of adsorption equilibria in a multi-metal, saturated system and also the adsorption kinetics of an unsaturated system. Analysis of each individual isotherm will enable a comparison with the analogous single metal isotherm system (Bezzina et al., 2020), determining the effect of multiple coexisting metals on the adsorption mechanisms and total capacity, together with the proposal of a new modified Langmuir isotherm, to successfully predict the effective saturation capacity for a given metal in a competitive system. This is accompanied by an in-depth analysis of adsorption kinetics for all metals in the multicomponent solution. To the best of our knowledge, these are the first experiments of their kind performed in an acetate matrix.

2. Methods

2.1. Reagents and stock solutions

All reagents were of analytical grade or higher. Copper chloride, iron (II) chloride, lead nitrate, sodium chloride, sodium hydroxide and zinc chloride purchased from Sigma-Aldrich (UK) apart from glacial acetic acid (VWR, UK). MTS9301 and C107E resins were kindly donated by Purolite (UK) and Lewatit MonoPlus TP214 by Lanxess (UK). All ion exchange resins were preconditioned by contact with H_2SO_4 (1M, 10 bed volumes), prior to washing with deionised water (50 bed volumes). 'Bed volume' refers to the minimum volume of water or solution required to fully wet the mass of an ion-exchange resin. Table S1 describes some of the characteristics of each resin, with functionalities shown in Fig. 2.

2.2. Metal uptake isotherms from acetic acid media

The purpose of the isotherm experiments was to calculate the effective capacities of MTS9301, C107E and TP214 for Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} in competitive conditions. Equimolar solutions negated the influence of equilibria and, therefore, molar ratios on adsorption reactions, allowing unambiguous orders of selectivity to be generated. Mixed metal solutions were generated from the appropriate metal salts

(200 mmol L^{-1} for each individual metal), ensuring that the number of ions in solution would be well above the saturation capacity of the adsorbents, at greater volumes. Each solution contained 0.5M acetic acid and 0.5M NaCl. Solutions were adjusted to pH 4.5 with NaOH.

2.3. Kinetic behaviour of metal uptake from acetic acid media

Kinetic experiments were undertaken to attain an understanding of the mechanisms and kinetic behaviour of metal-capture, with respect to each resin. Aqueous metal solutions for kinetic experiments again contained Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} (200 mg L^{-1} for each individual metal). Sample solutions were buffered and neutralised as previously described. Kinetic experiments were conducted over 24h. Ten 'thief' samples, of 1 mL, were taken between 0 and 24h. The overall solution volume did not change by >2% during the course of the experiments.

2.4. Analysis

Pre- and post-resin-contact samples were diluted appropriately, using 1% nitric acid (Trace Select grade, Fisher, UK), to produce an analyte concentration range of 1–10 mg L^{-1} . Analysis was performed using an AAAnalyst 400 Atomic Absorption Spectrometer (PerkinElmer, UK), using an air-acetylene flame and controlled by WinLab32 software, which quantified the concentration of each metal in the sample solutions. The instrument was calibrated for each metal with a blank and three standards appropriate for the analyte concentration range. Check standards were analysed at least every ten samples, to account for any instrumental drift. The analytical error values were calculated by measuring the pre-contact solution for each thermodynamic or kinetic experiment, followed by suitable propagation. All pH measurements used a Ag/AgCl electrode and four-point calibration.

3. Results

For each ion-exchange resin, the thermodynamic and kinetic uptake behaviour of the studied metals will now be presented. The Supporting Information shows results from the same experiments, with respect to percentage extraction; as a function of both the total number of moles of metal adsorbed (isothermal experiments) and as a function of time (kinetic experiments).

3.1. C107E

The isothermal extraction of copper, iron(II), lead and zinc by C107E is seen in Fig. 3. In this and all subsequent figures, the dotted lines represent the sequential increase in the starting quantity of each metal in solution. They are included for clarity; to illustrate the complexity in the adsorption behaviour in some cases. Error bars are included in all figures, but are sometimes too small to be seen. The copper, lead and zinc data display gentle initial isotherm slopes, indicating fairly weak adsorption. Copper and lead adsorption reach an experimental plateau at 0.8–0.9 mmol g^{-1} , without reaching saturation. Zinc reaches ~ 0.3 mmol g^{-1} without saturation. Unlike the other three metals, the iron(II)

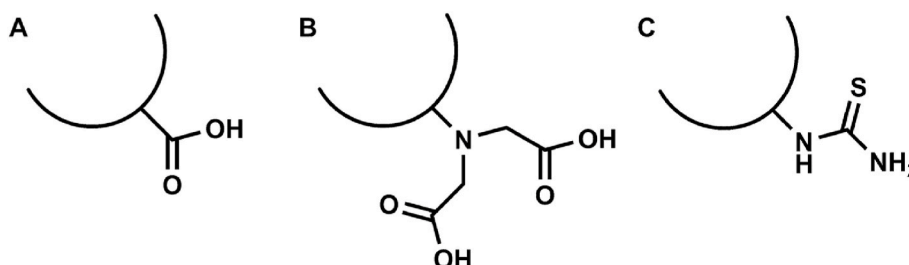


Fig. 2. Chemical structures of ion-exchange resin functionalities (A = C107E, B = MTS9301, C = TP214). Semicircles signify the adsorbent matrix.

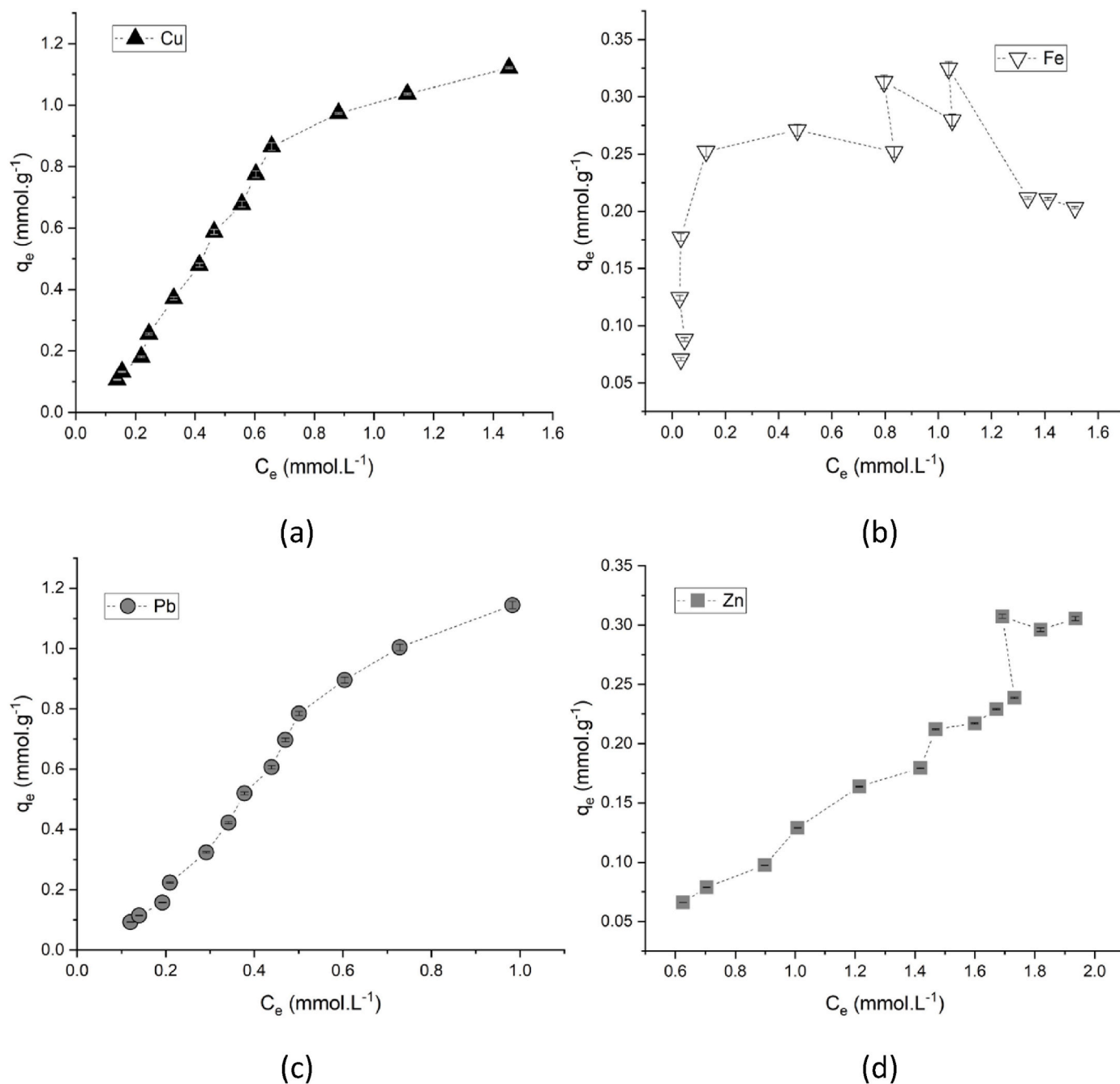


Fig. 3. Isothermal adsorption of copper (a), iron (b), lead (c) and zinc (d) by C107E in acetic acid media (initial concentration 200 mmol L⁻¹ per metal. T = 21 °C. Resin volume = 2 ml. Solution volume = 20–400 ml.

isotherm, shows a steep initial adsorption profile, yet with a low maximal capacity of $\sim 0.3 \text{ mmol g}^{-1}$, followed by a seeming desorption process. The iron(II) data was noisy compared to the other metals.

Kinetic data for C107E are shown in Fig. 4. Copper and iron(II) adsorption reaches equilibrium at $> 750 \text{ min}$, which is significantly slower than that of zinc and lead ($> 500 \text{ min}$). Again, C107E exhibits stronger affinity towards copper and lead (both reaching $> 75\%$ removal) than zinc and iron (Fig. S4).

3.2. MTS9301

The mixed-metal isotherm data for this resin is displayed in Fig. 5. Copper adsorption reaches a maximum of $\sim 1.6 \text{ mmol g}^{-1}$ with a rapid increase in q_e : C_e ratio until a capacity of $\sim 0.5 \text{ mmol g}^{-1}$, followed by a

shallower gradient. Data for the other 3 studied metals is remarkable, since they all reach distinct peak metal capacities, at various C_e values, before experiencing significant desorption. The adsorption of iron(II) reaches a maximum of $\sim 0.5 \text{ mmol g}^{-1}$, while lead and zinc uptake reaches a lesser value of $\sim 0.4 \text{ mmol g}^{-1}$.

The kinetic behaviour of MTS9301 is displayed in Fig. 6. The adsorption of copper equilibrates first and occurs in $\sim 300 \text{ min}$. The other 3 metals equilibrate rather more slowly, with the process complete in $> 500 \text{ min}$. The percentage extraction for all species was $\geq 90\%$ complete within the 24h contact period (Fig. S5).

3.3. TP214

The relevant isotherms for TP214 performance are shown in Fig. 7. It

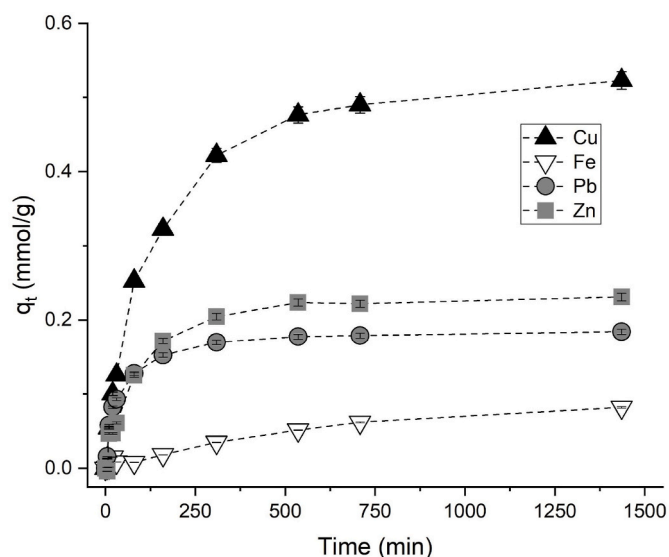


Fig. 4. Time dependent extraction of copper (a), iron (b), lead (c) and zinc (d) by C107E in acetic acid media (initial concentration 200 ppm, temperature 21 °C, 0.5M NaCl, 0.5M acetic acid, 10 ml wet settled resin, 500 ml solution).

can be seen that only the copper data takes a typical isotherm form and an experimental maximal capacity of $\sim 1.125 \text{ mmol g}^{-1}$ is reached. For the further 3 species, extraction was an order of magnitude lower and the data were generally noisy.

Results from the TP214 kinetic study are seen in Fig. 8. The high uptake of copper observed in the thermodynamic experiment is again repeated, although equilibrium is reached rather slower than for MTS9301, taking 500–750min. Iron(II) uptake was not significant, while both lead and zinc exhibit a high initial removal rate, but also a partial desorption process after 100min.

4. Discussion

4.1. Mixed metal isotherms

The isothermal metal extraction from the multi-species systems will now be discussed and rationalised, with respect to each resin. For C107E, the highest experimental capacities were for copper and lead ($\sim 1.2 \text{ mmol g}^{-1}$). The uptake of both metals gave rise to two discrete isothermal regions, which we postulate illustrates the conditions in which metal-proton-exchanges become dominated by metal-metal-exchanges. The adsorption of iron(II) reaches a maximum, plateaus, then decreases slightly over the experimental dataset, though with a high degree of scatter in the data at higher solution volumes. The observed maximum uptake is similar between iron(II) and zinc, both being an order of magnitude lower than for the other two metals. Dissimilarly, MTS9301 shows a clear preference for copper over the other competing species, which all undergo desorption in favour of further copper adsorption. This again creates a second delineated region of the copper isotherm, after the initial steep 'knee' of the isotherm. The reason this phenomenon is not observed for C107E is likely due to the significantly greater exchange capacity of this resin (Table S1). TP214 also has a clear affinity for copper, but also almost negligible uptake of the other metals. This is due to copper(II) and thiourea functioning as a REDOX couple, with the metal being reduced to copper(I) as part of the adsorption process (Mubarok and Irianto, 2016; Kotze et al., 2005; Bezzina et al., 2018, 2020; Harland, 1994). Essentially this deactivates the TP214 functional groups to further adsorption.

4.1.1. Attempted modelling with classical two-parameter isotherms

Thermodynamic data were fitted to a number of common, two-

parameter models; namely the Langmuir, Freundlich, Temkin and Dubinin-Radushkevitch (D-R) equations (Table 1) Fitting was achieved using non-linear least-squares regression. Such models have their theoretical origins in the description of adsorption of single gas-phase species and accordingly, there are limits to their validity in solid-phase/solution-phase systems. In this instance, further complexity is caused by the multi-species solutions used and ensuing competition for adsorption sites. Higher adsorbate concentrations lead to saturation of the resin and cause variation in mechanisms of uptake. These caveats are established in the literature. However, the isotherm models used can still offer valid insights into adsorption data. (Foo and Hameed, 2010; Ho et al., 2002; Robshaw et al., 2019a). There is a paucity of literature interpreting multi-metal isotherm systems of the kind studied here. However, comparisons can be made to an acetate system which investigated the uptake of each of the relevant metals in isolation of each other (Bezzina et al., 2020).

The Freundlich model can be used to indicate the heterogeneity of binding of the adsorbate. It returns the parameters a_F , which is a measure of adsorption capacity, and b_F , which indicates binding intensity. The Langmuir equation describes a monolayer adsorption phenomenon, with the parameter q_{max} (mol g^{-1}) indicating the monolayer saturation capacity and a_L (L mol^{-1}) being a Langmuir-specific constant. The Temkin model can describe binding energy for a system in which there is a linear relationship between the quantity of adsorbate bound and the enthalpy of adsorption (within certain adsorbate concentration ranges). The Temkin constant b_t (J mol^{-1}) relates to this heat of sorption and a_t is again a constant specific to the system. The D-R isotherm calculates both a saturation capacity (q_D , mol g^{-1}) and the constant, B_D , which relates to free energy of adsorption (E , kJ mol^{-1}) as follows (Equation (1)):

$$E = \frac{1}{\sqrt{2B_D}} \quad (1)$$

A common feature of all the models is that they all incorporate a parameter associated with the favourability of binding. For example, regarding the Freundlich b_F parameter, a value of 0 points to irreversible binding; ≥ 1 denotes unfavourable or cooperative binding and $0 < b_F < 1$ denotes favourable binding (Dada et al., 2012; Balarak et al., 2017). These parameters can be used to derive an order of affinity of metals, for all three resins, according to each isotherm model. These orders are shown in Table S6. Table S1 displays the full set of returned parameters from fitting to the Freundlich model. It should be noted that for all subsequent model-fitting data, we fitted the models to MTS9301 data in two ways: the first attempting to describe the whole dataset, the second attempting to describe the data only to the point where the experimental q_{max} was reached (in other words, before the desorption of other metals at the expense of further copper uptake). These truncated datasets are denoted as "reduced" in Tables S2–S5. Note that the truncation is not applied to copper data, as there was no apparent desorption of this species. Overall, the Freundlich isotherm fits C107E data well, with only iron(II) returning an R^2 value < 0.9 . The reduced MTS9301 dataset in general led to a much superior Freundlich model fit for all metals. For TP214, the deleterious copper(II) binding with the thiourea functionality (Doona and Stanbury, 1996; Kolodynska et al., 2009; Krzewski et al., 1980; Hubicki et al., 2007; Morcali et al., 2013) leads to insignificant adsorption of the other metals, returning an R^2 of 0.904 for copper. Iron(II) was the only other species for which a tentative R^2 value could be calculated and suggested a low intensity of binding. TP214 had a low capacity for copper, relative to C107E and MTS9301, which may be attributed to functional group loading (Table S1), but a greater binding intensity. Overall, the Freundlich isotherm was not an effective tool to describe the system, which is to be expected, as its purpose is to describe physisorption phenomena (Robshaw et al., 2019a).

The Langmuir displays similar goodness-of-fit to the Freundlich for copper and lead adsorption by C107E ($R^2 = 0.947$ and 0.949 , respectively, Table S3). The low affinity of the resin for zinc (Bezzina et al., 2020), led to highly scattered data and the values associated with this fit

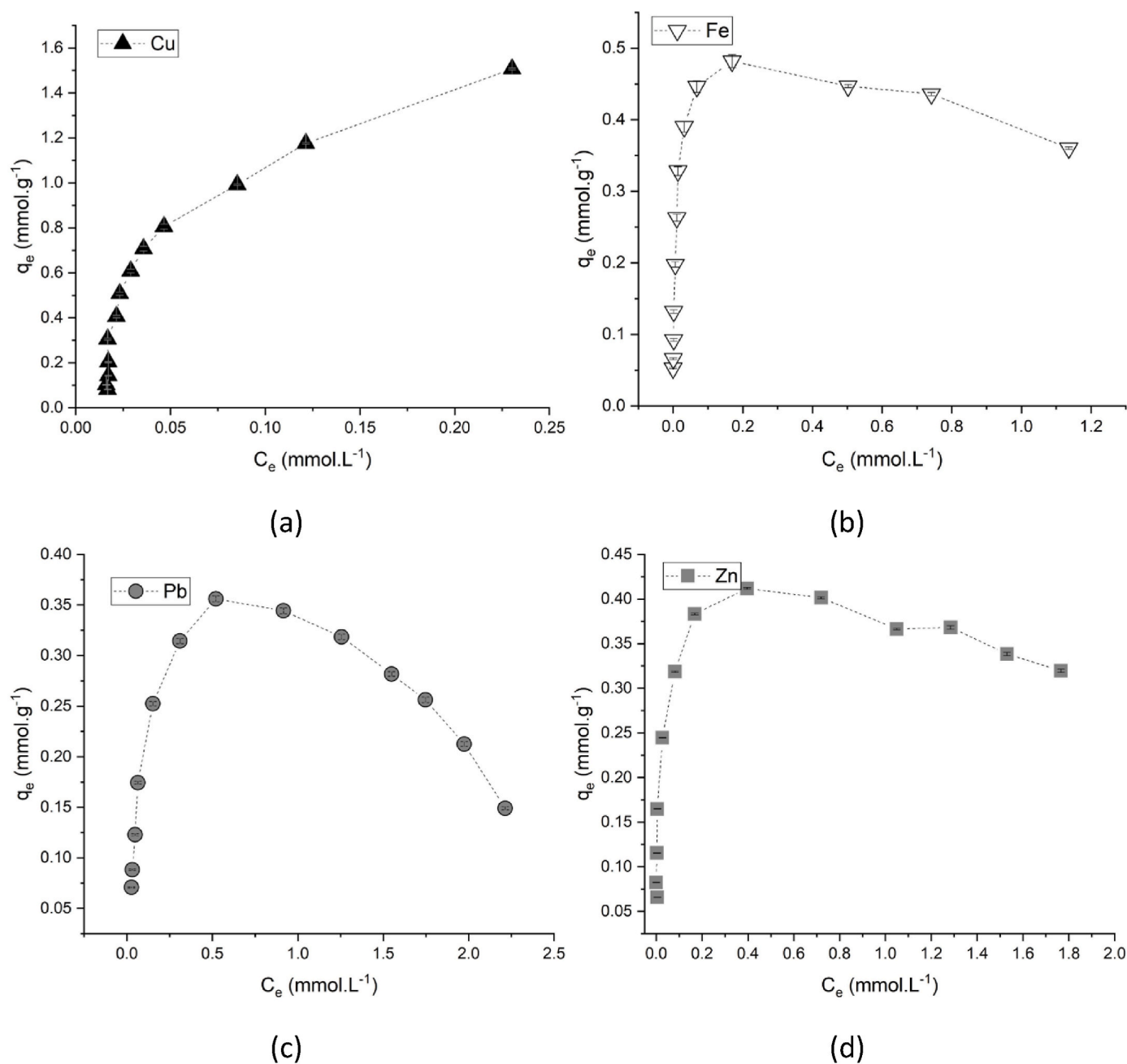


Fig. 5. Isothermal adsorption of copper (a), iron (b), lead (c) and zinc (d) by MTS9301 in acetic acid media (initial concentration 200 mmol L^{-1} per metal. $T = 21 \text{ }^\circ\text{C}$. Resin volume = 2 ml. Solution volume = 20–400 ml.

are meaningless. While lead adsorption returns a q_{max} value an order of magnitude higher than that of copper (0.01 ± 0.01 versus $0.0027 \pm 0.0006 \text{ mol g}^{-1}$), the associated error again renders the value somewhat meaningless. The Langmuir isotherm fits MTS9301 data for copper and the reduced dataset for iron(II) and lead quite well ($R^2 = 0.919$, 0.972 and 0.992 , respectively), but fails to describe zinc data well ($R^2 < 0.9$). The model q_{max} parameter for copper is $2.2 \pm 0.3 \times 10^{-3} \text{ mol g}^{-1}$, the highest of all the metals by an order of magnitude. The Langmuir model also fails to describe TP214 data except for copper, for which a q_{max} parameter of $1.1 \pm 0.1 \times 10^{-3} \text{ mol g}^{-1}$ is returned and also the highest value for a_L observed in this study. In general, while more accurate than the Freundlich, the Langmuir model is too simplistic to account for the array of proposed interactions, which collectively make up the uptake of the different metals.

The Temkin model provided a good description of C107E adsorption

of copper and lead, with R^2 values of 0.973 and 0.952 , respectively, while the fit for zinc is tentative ($R^2 = 0.895$) and for iron(II), non-existent (Table S4). For MTS9301, the Temkin model cannot describe the data for iron(II) or zinc (even with the reduced datasets), with copper and particularly the reduced lead dataset described well ($R^2 = 0.959$ and 0.994 , respectively). This model fits all TP214 data relatively poorly. Based on these data, it would not be accurate to state that there is likely a linear relationship between saturation and heat of sorption present within this system, which again, we attribute to the heterogeneous exchange processes at work.

The D-R isotherm adequately describes the uptake of copper, lead and zinc by C107E ($R^2 = 0.936$, 0.957 and 0.940 respectively), with a poor fit to iron(II) data (Table S5). The observed trend in capacity is $\text{Pb} > \text{Zn} > \text{Cu}$. However, the large extrapolation involved for the zinc isotherm results in a highly tentative maximal value. For MTS9301, the

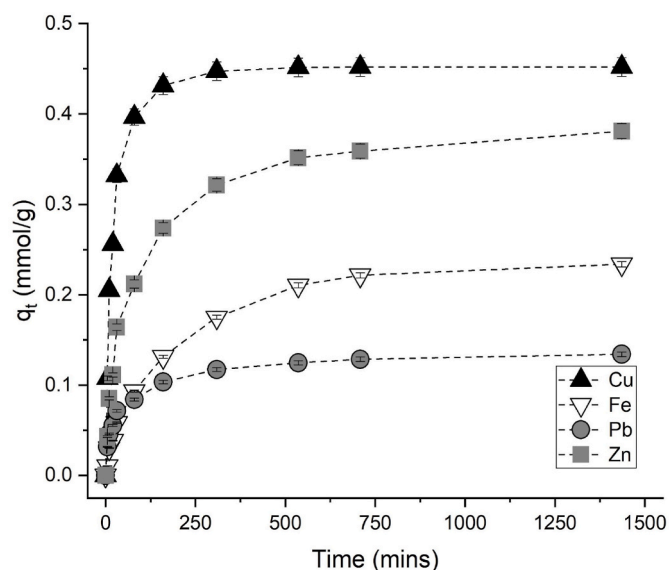


Fig. 6. Time dependent extraction of copper (a), iron (b), lead (c) and zinc (d) by MTS9301 in acetic acid media (initial concentration 200 ppm, temperature 21 °C, 0.5M NaCl, 0.5M acetic acid, 10 ml wet settled resin, 500 ml solution).

reduced datasets of iron(II) and lead fit the model reasonably well, whereas copper and zinc display a lower R^2 of ~ 0.89 . For TP214, we again observe only a tentative fit to copper data ($R^2 = 0.915$), returning a q_D value of $0.0034 \pm 0.0007 \text{ mol g}^{-1}$, which is somewhat in excess of that recorded experimentally. Nonetheless, the calculated desorption free energy is within experimental error of that recorded for the equivalent experiment with no competing metals (16 ± 1 and $17 \pm 1 \text{ kJ mol}^{-1}$) (Bezzina et al., 2020). This large value clearly indicates a chemisorption phenomenon (Bezzina et al., 2019; Doona and Stanbury, 1996; Kolodynska et al., 2009; Krzewska et al., 1980). The model did not describe the data for other metals well.

Compared to previous reports, the general intensity of binding, demonstrated in this work, is of low magnitude. For example, for copper uptake by C107E, the derived desorption energy (from the D-R model) was $\sim 0.7 \text{ kJ mol}^{-1}$ below an equivalent system with copper as the only metal present ($7.7 \pm 0.4 \text{ kJ mol}^{-1}$ vs $8.4 \pm 0.4 \text{ kJ mol}^{-1}$) (Bezzina et al., 2020; Lin and Juang, 2005). The MTS9301 data indicated an even more significant reduction in desorption energy, compared to our own single-metal system ($9.8 \pm 0.6 \text{ kJ mol}^{-1}$ vs $14 \pm 1 \text{ kJ mol}^{-1}$) (Bezzina et al., 2020) and other strong acid matrices reported (Bulai et al., 2009; Bleotu et al., 2018; Pehlivan and Altun, 2007). The competing metals and presence of the acetate complexant are seemingly influencing the binding affinity, compared to more simple sample matrices. A strongly heterogeneous binding mechanism is therefore proposed, which can be observed in the pseudo-two-stage adsorption profiles, seen most clearly in Fig. 3a, c and 5. This is proposed to indicate the prevalence of metal-metal exchange, rather than proton-metal exchange as saturation increases. The effect is more pronounced than for C107E, as this adsorbent does not reach capacity in these experimental conditions; the competition between metals being therefore lesser.

Within this, it is notable that the Freundlich b_F parameters for all experiments were $\gg 0$, implying physisorption. However, it is feasible that the progression of proton-metal exchange to metal-metal exchange results in the isotherm possessing a pseudo-physisorption character and may simply imply heterogeneous binding (Lin and Juang, 2005).

Another obvious feature of the data is how the capacity of the resins for lower-affinity species is reduced. For MTS9301, use of the reduced dataset reveals the low capacity of the resin for lead ($q_{\text{max}} = 0.43 \pm 0.02 \text{ mmol g}^{-1}$) in the presence of copper. This value is only $\sim 20\%$ of the recorded capacity in strong acid conditions (Liu et al., 2009). Similarly,

for C107E, the observed saturation capacity for zinc we recorded here was reduced by an order of magnitude compared to single-metal conditions (Bezzina et al., 2020). The performance was still further reduced in comparison to strong acid conditions (Lin and Juang, 2005; Pehlivan and Altun, 2007).

4.1.2. Enhanced modelling of the multi-metal system with a modified Langmuir model

Due to heterogeneous uptake mechanisms and (particularly) the observed desorption phenomena in the case of MTS9301 data, it is clear that the classical two-parameter isotherms are incapable of modelling these data. As seen in Table S6, the derived binding affinities that result from the modelling, particularly for MTS9301, are dubious: copper is predicted to have low affinity, even though it displaces all other metals in competitive binding. There have been previous efforts to model these systems, accounting for multiple metal species (Misak, 1993; Allen and Brown, 1995; Choy et al., 2000). Specifically, employing an extended Langmuir model (Choy et al., 2000), it is theoretically possible to fit data in conditions with an infinite number of adsorbate species. Nonetheless, this model is based on an initial fitting to single-metal isotherms and cannot account for a system where significant desorption takes place.

Thus, a modification to the Langmuir model was proposed. Because the data for a single metal species, in saturated multi-metal conditions, is parabolic in character, a single constant can be added to the Langmuir equation, to better describe the partial desorption of that species (Equation (2)):

$$q_e = \frac{q_m a_L C_e}{1 + a_L C_e} + \text{des} \quad (2)$$

where 'des' is an empirical and unitless parameter, which describes a concentration-dependent level of desorption. We emphasise that this parameter has no theoretical origin; it is simply a tool used to better describe the adsorption data within the experimental parameters studied, for systems undergoing competitive desorption processes. While this modification cannot account for competition between specific metals (although this would be the case in binary metal systems), it should be able to describe a system which has high competition for binding sites between metals and where one species has significantly more affinity for the adsorbent active sites than the others. Despite the possibility of a better description of the data, it is noted that the more parameters included in a function, the less meaning can be assigned to each parameter. Nonetheless, it can be stated unambiguously that the larger the 'des' parameter, the more pronounced is the desorption of the species in question, in favour of higher affinity species. Therefore, this section is devoted to the use of the desorption-modified Langmuir to account for the metallic adsorption observed.

The parameters derived from this proposed model for metal uptake behaviour of both C107E and MTS9301 are shown in Table 2. Due to the negligible removal of iron(II), lead and zinc by TP214, these experiments are not included in the desorption-modified Langmuir dataset. It can be seen by comparing Table 2 and Table S3 that the 'des' parameter inclusion allows more successful modelling of the full datasets across all experiments. The copper and lead C107E data in particular are well accounted for by the desorption-modified isotherm. MTS9301 data also featured improved R^2 values in comparison to the unmodified Langmuir model.

Practically, the calculated q_{max} values for copper adsorption to C107E, derived from the desorption-modified Langmuir model, are more realistic than those calculated by the unmodified variant, which are beyond the known operating capacity of the resin (Tables S1 and S3). They do however require extrapolation. In a practical sense, the calculated 'des' parameters indicate that C107E is unlikely to desorb lead in an acetate matrix, and that MTS9301 is unlikely to desorb copper. This is significant for liquors with 'preg-robbing' capabilities, which would be the case in the proposed context (Kotze et al., 2005).

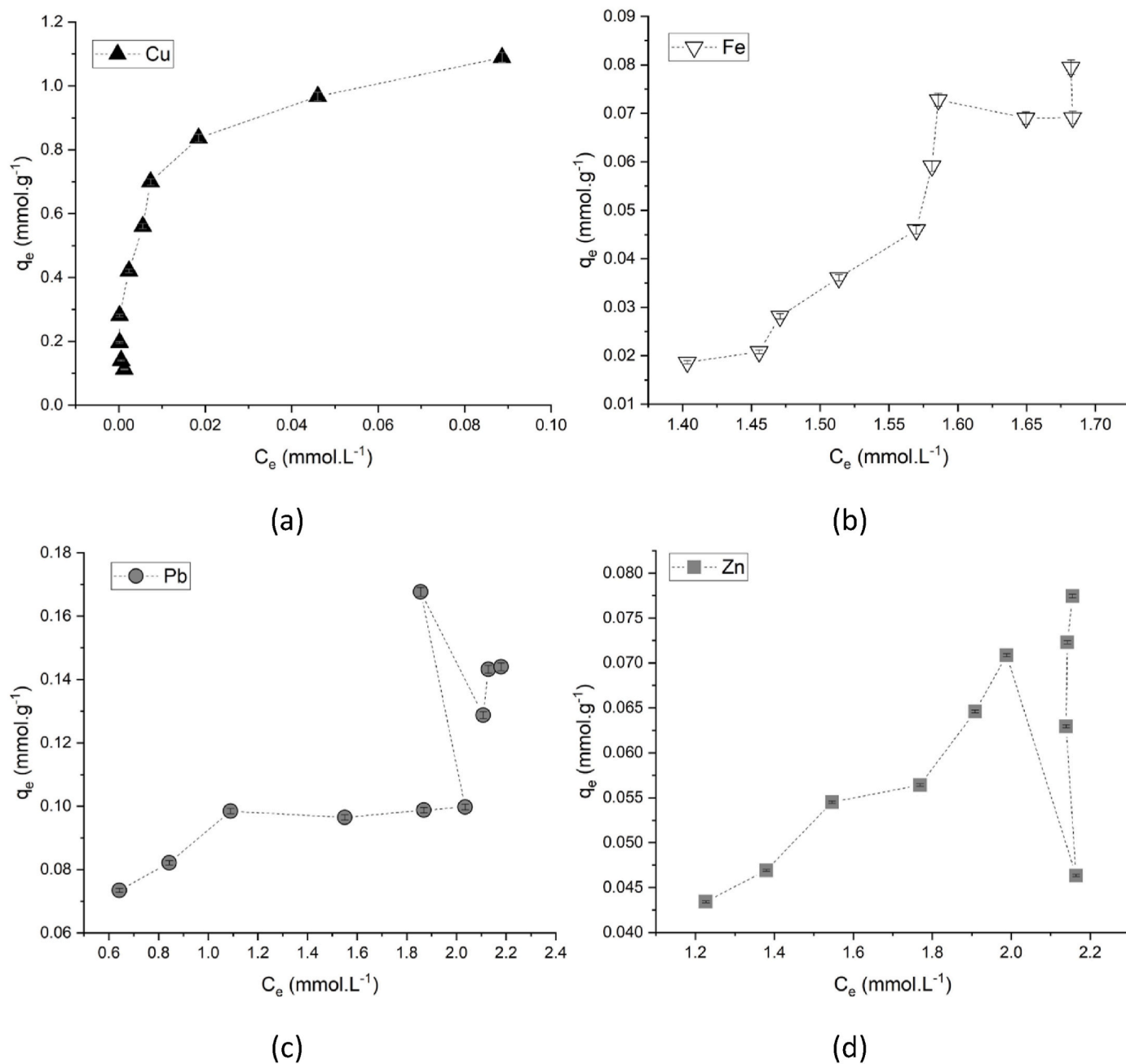


Fig. 7. Isothermal adsorption of copper (a), iron (b), lead (c) and zinc (d) by TP214 in acetic acid media (initial concentration 200 mmol L^{-1} per metal. $T = 21 \text{ }^\circ\text{C}$. Resin volume = 2 ml. Solution volume = 20–400 ml.

With respect to C107E adsorption of iron(II), as previously mentioned, there is a large amount of scatter within the data. Therefore, the desorption-modified Langmuir model does not improve the fitting in this instance. However, the MTS9301 iron(II) isotherm was described well by this model and it accurately predicts the experimentally-observed q_{max} ($0.482 \pm 0.009 \text{ mmol L}^{-1}$) with a value of $0.49 \pm 0.03 \text{ mmol g}^{-1}$.

The predicted capacity of C107E for lead in the multi-metal system by the desorption-modified Langmuir model is significantly extrapolated and a far higher capacity is predicted than for single-metal conditions. Nevertheless, the adsorption does appear to increase beyond the experimental range (Fig. 3) and ultimate capacities are hard to predict. C107E has the higher affinity for lead, indicated by the lowest desorption constant of all the metals. There was observable desorption of lead from MTS9301, with the desorption constant being similar to that for

iron(II) and zinc.

Similarly to iron(II), no meaningful results could be attained for the adsorption of zinc by C107E, even with the modified Langmuir model, due to weak interactions. Zinc adsorption by MTS9301 however returned a good fit. Zinc underwent the greatest desorption from MTS9301, with a desorption constant of 1.6 ± 0.1 , suggesting extraction would be problematic from real sewage sludge, due to competition from other cations (Westerhoff et al., 2015).

Although the model adequately accounted for the relative degrees of desorption of the metals from the functionality, it was not as successful in being able to describe the proposed shift in uptake mechanism from metal-proton to metal-metal exchange for the higher affinity metals. Furthermore, the ‘des’ parameter will almost certainly be influenced by the molar ratios of the aqueous metals, since the systems heavily rely on equilibria. The model is hence ‘situational’ and has only been proven for

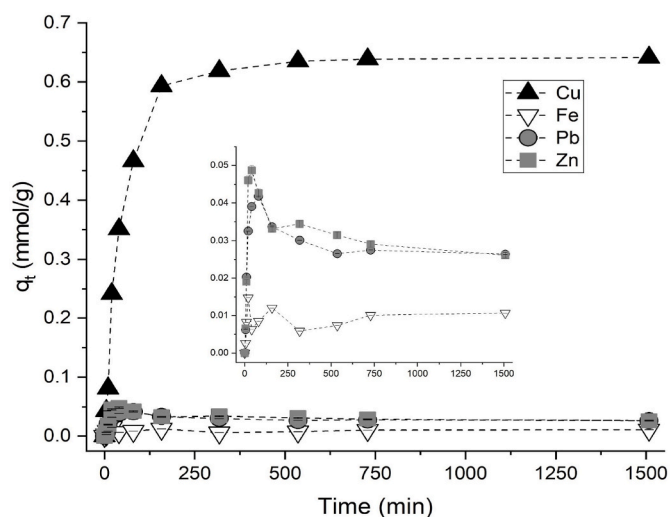


Fig. 8. Time dependent extraction of copper (a), iron (b), lead (c) and zinc (d) by TP214 in acetic acid media (initial concentration 200 ppm, temperature 21 °C, 0.5M NaCl, 0.5M acetic acid, 10 ml wet settled resin, 500 ml solution).

Table 1
The unmodified two-parameter isotherm models used initially to describe the adsorption.

Model name	Equation form
Freundlich	$q_e = a_F C_e^{b_F}$
Langmuir	$q_e = \frac{q_m a_L C_e}{1 + a_L C_e}$
Temkin	$\frac{q_e}{q_m} = \frac{RT}{b_T} \ln(a_T C_e)$
D-R	$q_e = q_D \exp\left(\frac{-B_D [RT \ln(1 + \frac{1}{C_e})]^2}{C_e}\right)$

Table 2
Variables obtained by fitting the mixed metal concentration dependence data of C107E and MTS9301 to the desorption-modified Langmuir isotherm model.

Resin	Values	Copper	Iron(II)	Lead	Zinc
C107E	aL	17 ± 5 × 10 ²	12 ± 5 × 10 ³	10 ± 3 × 10 ²	–
	Qmax	2.1 ± 0.1 × 10 ⁻³	4.0 ± 0.6 × 10 ⁻⁴	3.0 ± 0.5 × 10 ⁻³	–
	Des	3.0 ± 1 × 10 ⁻⁴	1.39 ± 0.07	2.7 ± 0.8 × 10 ⁻⁴	6 ± 7
	R ²	0.983	0.790	0.982	0.936
	MTS9301	aL	6 ± 3 × 10 ⁴	13 ± 2 × 10 ⁴	66 ± 6 × 10 ²
Qmax		2.8 ± 0.6 × 10 ⁻³	4.9 ± 0.3 × 10 ⁻⁴	5.1 ± 0.2 × 10 ⁻⁴	4.1 ± 0.3 × 10 ⁻⁴
Des		1.2 ± 0.7 × 10 ⁻³	1.4 ± 0.1	1.37 ± 0.01	1.6 ± 0.1
R ²		0.965	0.976	0.990	0.912

the system studied in these particular experiments. There may be a practical application for the model (with further development) in the prediction of complete desorption of weaker-bound species in favour of stronger-bound in a saturated system. In the case of copper adsorption by MTS9301, it would be useful to know the concentration of the liquor at which complete desorption of all other species in favour of copper is reached, as this would allow thermodynamic separation at high metal concentrations and reduce the need to pump and treat large volumes of aqueous waste.

In an attempt to rationalise the desorption behaviour reported, we investigated the relationship of the empirical ‘des’ constant with the physicochemical and thermodynamic properties of the relevant metal

ions (Table S12). Because of the small number of datapoints, any trends are very tentative. In general, there was no relationship between the ‘des’ parameter and metal ion properties, with the interesting exception of the ΔS value for the formation of the relevant metal acetate complex. This value is higher for the copper acetate complex (~93 J mol⁻¹) than for the equivalent lead and zinc complexes (~58 J mol⁻¹). Hence the desorption of copper would be predicted to be more entropically favourable. However, the reverse is true (Fig. S7), which suggests that adsorption of copper to MTS9301 is even more entropically favourable than formation of the free acetate complex. A possible explanation is that adsorption of a copper species by one iminodiacetic acid moiety displaces one or more acetate ligands into the surrounding solution, whereas lead and zinc bind by simply incorporating the iminodiacetate group into the bound ternary complex (i.e. ligands are not displaced); the reaction being thereby less entropically favourable. In support of this, previous HySS modelling of the single-metal systems (Alderighi et al., 1999) predicted the dominant copper solution-phase complex as a mixture of Cu(Ac)₂ and Cu(Ac)₃, while the dominant lead and zinc species are less acetate rich.

4.2. Kinetics

The kinetic experiments resulted in fairly linear and predictable adsorption data, in the case of both C107E and MTS9301. Equilibrium is reached for the uptake of all metals, with this occurring much more quickly for MTS9301 than C107E. TP214 exhibited rapid adsorption of copper and minimal affinity for the other species, concurrent with thermodynamic data.

The data were fitted to a number of well-known kinetics models; these being particle diffusion, film diffusion, Elovich, Lagergren and pseudo-2nd-order (Table 3). Fitting again employed a non-linear, least squares method. Such an exercise is useful in assessing the rate-limiting adsorption step, in describing reverse reaction behaviour and in calculating operational parameters relevant to engineering applications (Robshaw et al., 2019b). For all models, q_t refers to the concentration of a given adsorbate on the adsorbent at a given time (mmol g⁻¹).

The particle and film diffusion models can describe kinetic behaviour rate-limited (respectively) by either diffusion within the pore network of a particle, or through a stagnant, hydrous film at the solid-solution interface. For these models, k_{PD} and k_{FD} are respective particle and film diffusion rate constants, while C is a constant describing the thickness of the boundary film layer (Tarawou and Young, 2015). The Elovich model describes heterogeneous binding, accounting for both forward and backward binding reactions via the desorption constant β (g mol⁻¹) and initial sorption rate α (mol g⁻¹ min⁻¹) (Aharoni and Ungarish, 1976; Ho, 2006).

The Lagergren pseudo-1st-order and pseudo-2nd-order models can determine an array of useful parameters, these being pseudo rate con-

Table 3
Two-parameter single-metal isotherm models used within this study.

Name	Model
Particle Diffusion	$q_t = k_{PD} \frac{1}{t^2} + C$
Film Diffusion	$q_t = q_e (1 - e^{-k_{FD} t / 2.303})$
Elovich	$q_t = \frac{1}{\beta} \ln(t + \frac{1}{\alpha\beta}) + \frac{1}{\beta} \ln \frac{1}{\alpha\beta}$
Lagergren	$q_t = q_e (1 - e^{-k_1 t})$
Pseudo-2 nd -Order	$q_t = \frac{q_e^2 kt}{1 + q_e kt}$

stants, the initial adsorption rate and the reaction half-life ($q_e = 1$, $q_t = 1/2$) (Ho, 2006; Ho and McKay, 2002). The Lagergren half-life is calculated by:

$$t_{1/2} = \frac{0.693}{k_1} \quad (3)$$

with k_1 being the pseudo-1st-order rate constant. For the pseudo-2nd-order model, the initial rate of reaction (h_0 , $\text{mmol g}^{-1} \text{min}^{-1}$) and half-life of the reaction (Ho and McKay, 2002; Wu et al., 2009) are found from the following equations, with k_{2nd} being the pseudo-2nd-order rate constant):

$$h_0 = k_{2nd} q_e^2 \quad (4)$$

$$t_{1/2} = \frac{1}{k_{2nd} q_e} \quad (5)$$

In general, the kinetic data does not fit the particle diffusion model well (Table 4), with only iron(II) uptake by C107E achieving a reasonable R^2 of 0.968. The most likely explanation is that the macroreticular nature of all three resins allows rapid access of the liquor through the pores of the resin particles. While agitation of the RIP and large particle pore size will prevent intra-particle concentration gradients, the resin bead surface inevitably acquires and maintains a stagnant film, facilitated by the degree of surface charge (Harland, 1994). Diffusion through the film layer is hence limited by the concentration gradient between film and bulk solution (Tarawou and Young, 2015). This phenomenon resulted in more accurate fitting for the film-diffusion model in all circumstances (Table 4), with R^2 values > 0.95 . Notable exceptions were uptake of lead by MTS9301 and uptake of iron(II), lead and zinc by TP214. The REDOX interaction between copper and the thiourea functionality results in low kinetic hindrance of the Nernst film layer (Hubicki et al., 2007; Morcali et al., 2013).

With the application of the Elovich equation, for C107, all metal uptake results in an R^2 value > 0.96 (Table 4). Copper, lead and zinc had high rates of adsorption, with iron(II) an order of magnitude lesser, resulting in the trend of $\text{Pb} > \text{Cu} > \text{Zn} \gg \text{Fe}$ (Table S9). However, the trend in desorption rate ($\text{Pb} \gg \text{Fe} > \text{Zn} > \text{Cu}$) does not completely mirror the adsorption rate trend, with lead standing out as an anomaly. Desorption rate appears to correlate to ionic radius (Fig. S14).

MTS9301 kinetics were well described by the Elovich model (Table 4). The initial rates of adsorption are considerably higher than for C107E, with the trend being $\text{Cu} \gg \text{Pb} \approx \text{Zn} \gg \text{Fe}$, confirming the strong affinity of the resin for copper. Again, TP214 data were not described well by the Elovich model, with very poor fits for all metals except copper. Comparing MTS9301 and TP214 performance for copper extraction, the TP214 initial rate is lower, but it also features a much lower desorption rate.

Table 4
Summary of goodness-of-fit (R^2 values) of all kinetic models for multi-metal adsorption by the three resins.

Resin	Kinetic model	Copper	Iron	Lead	Zinc
C107E	Particle diffusion	0.883	0.968	0.741	0.824
	Film diffusion	0.989	0.977	0.965	0.987
	Elovich	0.986	0.975	0.965	0.963
	Lagergren	0.989	0.977	0.965	0.987
	Pseudo-2nd-order	0.998	0.976	0.991	0.989
MTS9301	Particle diffusion	0.589	0.916	0.792	0.840
	Film diffusion	0.986	0.983	0.918	0.958
	Elovich	0.930	0.991	0.992	0.989
	Lagergren	0.986	0.983	0.918	0.958
	Pseudo-2nd-order	0.997	0.994	0.973	0.990
TP214	Particle diffusion	0.685	0.151	0.094	0.046
	Film diffusion	0.990	0.542	0.783	0.691
	Elovich	0.920	0.384	0.461	0.374
	Lagergren	0.990	0.542	0.783	0.691
	Pseudo-2nd-order	0.983	0.476	0.677	0.572

The Lagergren model described C107E data reasonably well, according to the generated R^2 values (Table 4), but only predicted accurate q_e values for copper and zinc (the model parameters being within experimental error of the experimental values). Similarly, applying the model to MTS9301 data resulted in reasonable fits for all metals except lead. Similarly to other models, copper uptake is the only data well accounted for TP214, with the modelled q_e value within experimental error of the observed value.

For copper and lead extraction by C107E, the pseudo-2nd-order model resulted in better R^2 values than the Lagergren, while for iron (II) and zinc, the reverse was true (Tables S10 and S11). The corresponding q_e predicted and experimental values reinforced this. The derived half-lives from this model are greater than those for the Lagergren model. The apparent affinities (derived from the h_0 parameter) follow the trend of $\text{Pb} > \text{Cu} > \text{Zn} \gg \text{Fe}$. For MTS9301, we again see superior R^2 values to the Lagergren model (> 0.99 for copper, iron(II) and zinc; 0.973 for lead) and the majority of predicted q_e values were within experimental error of the observed values, with only iron(II) deviating significantly, though still $< 10\%$. The associated half-life values were similar to those returned by the Lagergren model, although the initial rate of reaction trend is different, with zinc this time suggesting faster adsorption than lead ($\text{Zn} > \text{Pb} > \text{Cu} > \text{Fe}$). Fitting of TP214 kinetic data for copper to the pseudo-second order model resulted in similar accuracy of description to the Lagergren model and a model q_e within $\sim 10\%$ of the experimental value.

With respect to copper uptake, the kinetic parameters returned for MTS9301 are at least one order of magnitude higher than for C107E. The faster adsorption can be rationalised by the chelating properties of the iminodiacetic acid, which would facilitate the exchange of two acetate ligands from the solution-phase complex and induce more rapid binding, probably aided by lone pair donation from the nitrogen atom (Selvakumar et al., 2006; Gao et al., 2014). In contrast, the binding to C107E can essentially be thought of as the simple exchange of a solution-phase acetate ligand for a solid-phase acetate ligand. Hence, the only factor that makes the reaction energetically favourable is the adsorption process itself (Marsh and Rodríguez-Reinoso, 2006).

In general, the metal uptake is described more successfully by the pseudo-2nd-order model, rather than the Lagergren. This is often inferred in the literature to imply a chemisorption, rather than physisorption mechanism is taking place (Robshaw et al., 2019a, 2020a). It may suggest that the aqueous metal complexes bind via ligand-exchange, rather than addition of a further ligand from the adsorbent to the complex and this is generally supported by the binding energies observed (Bezzina et al., 2020), with some previously noted exceptions.

An interesting feature of the data in general was that many of the kinetic parameters extracted, particularly for the pseudo-2nd-order model, could be correlated to the ionic radii of the respective metal ions (Table S13). This is perhaps surprising, because previous HySS modelling (Bezzina et al., 2019, 2020) has shown that the dominant solution-phase complexes formed by the ions are not equivalent. In other words, the size of the actual metallic species formed in solution bears little relevance to their ionic radii. The most prevalent respective species are $\text{Cu}(\text{Ac})_2$, Fe^{2+} , $\text{Pb}(\text{Ac})_2$ and $\text{Zn}(\text{Ac})^+$ (Alderighi et al., 1999), from which it might be predicted that iron(II) would exhibit the fastest rate of adsorption. Yet this is not the case, although lead does demonstrate the slowest adsorption, while also being the largest solution-phase species (Fig. S14).

The data is most likely related to steric factors. For example, in the case of adsorption of the metals by MTS9301 (Fig. S14b) it can be seen that the kinetic favourability of adsorption is very similar for Cu, Fe and Zn, but rather lesser for Pb. This is likely due to the smaller ions being able to fit into the iminodiacetic acid cavity (Gao et al., 2014), whereas the lead ion would bind outside the plane of the ligand, resulting in no interaction from the nitrogen atom. In contrast, for C107E (Fig. S14a), the larger size of the lead ion has a much less pronounced effect on the

adsorption kinetic favourability.

In comparison to previously-published work on the uptake of heavy metals, the adsorption kinetics seen in this work are slow. In studies on the uptake of copper by another iminodiacetic acid resin, the calculated h_0 values from the pseudo-2nd-order equation were an order of magnitude higher than we observed, being 0.025–0.032 mmol g⁻¹ min⁻¹ (Bulai et al., 2009). Two further commercial iminodiacetic acid resins were compared for adsorption of copper and lead and equivalent h_0 values were calculated as 0.02–0.05 mmol g⁻¹ min⁻¹ (Ling et al., 2010). Very fast rates of adsorption have been observed within sulphate media at pH 4 (pseudo-2nd-order half-life = 3.6min) (Bleotu et al., 2015). In all these cases, single-metal solutions, without complexant were used for the tests. It is therefore likely that the high acetate concentration in these experiments alters the chemistry of the film diffusion layer and makes diffusion of the adsorbate less favourable. This is of significance from an application perspective.

4.3. Application implications and overall resin comparison

The practice of fitting models to isothermal and kinetic data is practically the most useful for quantifying adsorbent capacities, indicating competitive behaviour between adsorbate, and determining operational parameters, such half-lives and rates. All such data can be used to assess the suitability of each resin for application in the previously-mentioned RIP process. In doing so, it is worthwhile to consider the necessity of removal of each species from sewage sludge to keep the resulting wastestream within allowed limits, with respect to metal concentrations. In the context of this work, the most relevant legislation is the EU Council Directive 86/278/EEC (European Union, 1986), which imposes limits of 1750, 1200 and 4000 mg kg⁻¹ for copper, lead and zinc respectively. Although the initial focus is removal, it is also worth noting that the current market values of these three pure metals, at the time of writing, were £7560, 1720 and 3120 per tonne (London Metal Exchange cash offer price on 01 June 2022). Therefore, while substantive removal of copper, lead and (to a lesser extent) zinc is necessary for the safe use of sewage sludge as a fertiliser, the greatest economic value, lies mainly in copper and zinc recovery. We also note that the acetate salts of these three metals have no widespread commercial usage. Since there are no legislative limits in iron concentration in fertiliser slurry (European Union, 1986), the ‘ideal’ adsorbent would target the three more toxic metals, with iron being a much lesser consideration. In fact, it would be desirable that as little iron as possible is taken up by the chosen adsorbent, as it would decrease its efficiency in adsorbing the target heavy metals.

In general, this work has showed some of the complexities of attempting metal extraction from a multi-component system. Because of competition for binding sites, the adsorption of all species tends to be weaker and more reversible than for the equivalent single-metal experiments. The kinetics of adsorption are also significantly retarded, which has implications for the feasibility of the intended system.

With respect to the equilibrium data presented here, the model parameters reported (for example q_e values) will mainly not be transferable to real sewage sludge leachates. This is because they are specific to the initial metal concentrations used and as mentioned, the associated equilibria are concentration dependent. This is one of the complexities of trying to predict the behaviour of a multi-component system. This said, the development of the modified Langmuir to more successfully describe multi-metal isotherms is of significance to the application. In practice, the design of a RIP process would require the optimum ratio of resin to leachate to be found (in other words, the point at which close to the full exchange capacity of the resin is used and desorption of target metal species is minimised). This would likely be achieved with small-scale batch ‘scoping’ experiments and the generation of isotherms. The knowledge that the isotherms for individual metals can take a parabolic shape is important, as in practice, it would allow rapid identification of the ideal resin:leachate ratio. Using the modified Langmuir

model, only a small number of datapoints would be needed to ascertain the peak of the parabola for each metal (whereas the unmodified models would fail to do this). Data for all metals could then be compared to establish the optimum resin:leachate ratio. As we have seen, the heavy metal composition of different batches of sludges is highly variable, so considerable plant processing time could be saved in this manner.

In terms of kinetic parameters, the adsorption half-life is perhaps the most important from an environmental engineering perspective. This is because (providing metal adsorption data fits a given model well), this parameter can be used to estimate the residence time required for the RIP process. This has obvious techno-economic implications, in terms of how much sludge and leachate can be effectively treated in a given length of time. This is one of the advantages in generating adsorption data for a more realistic, multi-component system. In this work, the pseudo-2nd-order half-lives of copper, iron(II) and zinc are all greater for C107E than for MTS9301 which, as mentioned, we attribute to the stronger chelating interaction being present for the smaller metal ions. However, the larger lead ion returned similar half-lives for both C107E and MTS9301 (Tables S10 and S11). Indeed, the values were similar to those recorded for IRC748, a commercially available resin with an iminodiacetic acid functionality, in experiments conducted in a non-complexing media (Ling et al., 2010). The variable impact of the acetate complexant on binding with a carboxylic acid functionality can be seen in a strong inverse correlation between the initial rate of reaction and enthalpy change of the relevant acetate complex formation (Fig. S11). C107E clearly has high affinity for lead and copper, with neither undergoing significant competitive desorption in the mixed metal conditions studied, and capacities, not dissimilar to those achieved in a strong acid system (Liu et al., 2009; Fu et al., 2014). However, the resin did not reach saturation within the experimental conditions used, and while capacities appeared high, the extraction percentages decreased dramatically with increasing solution volume (Fig. S1). The resin performed poorly for both iron(II) and zinc and although the lower extraction percentages are advantageous with respect to iron(II), zinc extraction is a definite requirement for the RIP system (European Union, 1986).

As we have seen in comparison to previous literature (Ling et al., 2010), the adsorption kinetics of the iminodiacetic acid group seem to be hindered by the challenging aqueous conditions studied. However, MTS9301 was kinetically superior with respect to copper, iron(II) and zinc, whilst being approximately equal to C107E for lead uptake. The overall capacity of the resin for copper was not affected by the complexant, being similar to reported literature values (Lin and Juang, 2005; Bulai et al., 2009; Bleotu et al., 2015). In contrast, the mixed metals environment significantly decreased MTS9301 capacity for lead, iron and zinc in comparison to previously-reported values (Lin and Juang, 2005; Li et al., 2011).

MTS9301 was however the most effective extractant overall, in terms of its ability to facilitate a high extraction % of copper lead and zinc from the initial volumes of solution (Fig. S2). Assuming > 90% extraction of each metal (without competition) can be maintained, 1 mL of wet settled resin is theoretically able to extract 0.365 mmol metal from solution. At capacity, the loaded resin would enjoy a total metal concentration of 2.729 ± 0.007 mmol g⁻¹, which is actually rather greater than the figure calculated from manufacturer capacity data of 2.21 mmol g⁻¹ resin.

A further potentially useful feature of the MTS9301 data was that the pseudo-2nd-order half-life of iron(II) was almost ten times that of copper, five times that of lead and nearly three times that of zinc (Table S11). This implies that a kinetic separation of the three target metals would be possible in the instance of high iron concentrations.

TP214 was poorest performer overall, failing to extract any metal apart from copper, whilst removal of this species was slower than for MTS9301 (half-life of 35 ± 3 min verses 14.1 ± 0.9 min). This highlights the value of working with multi-metal systems, as in idealised conditions, the functionality is known to uptake both iron (Dai et al., 2012; Kaveeshwar et al., 2018; Cavus et al., 2016) and lead (Liang et al., 2013;

Benkhatou et al., 2016; Wang et al., 2016). Although ~100% extraction of copper is achieved across all experimental conditions studied, the resin does not extract >75% of any other metal species. While this presents an attractive solution for selective removal of copper, with the hypothesised system, the simpler approach would be simultaneous removal of all target species and therefore TP214 is a less appropriate option. Given that copper is the most potentially valuable component in the sewage sludge leachate, there may be value in a process where a copper-selective resin is used in conjunction with a further 'pull-all' adsorbent. It is worth noting that the behaviour of TP214, with respect to copper uptake was the least affected by the presence of the other ions (Bezzina et al., 2020). However, in this scenario, the two resins would have to be separated by size-exclusion or differences in density, to allow elution of metals and downstream processing. This is by no means an easy design process and would add complexity to the engineering (Gopalakrishnan et al., 2012). Even in this case, the irreversible REDOX binding would not be amenable to multiple loading and eluting cycles and in this case, a copper-selective, but non-reducing resin, such as DOWEX M4195 would be a better choice (Robshaw et al., 2020b).

5. Conclusions

We have comprehensively investigated multi-metal isotherm and kinetic uptake of copper, iron(II), lead and zinc from an acetic acid medium by three ion-exchange resins, with a view to a resin-in-pulp (RIP) system for extraction of toxic metals from sewage sludge and subsequent valorisation as a source of phosphate. Attempts to describe the competition of metals for binding sites have been made via classical single-species adsorption models and the formulation of a rudimentary multi-metal adsorption isotherm model. Kinetic parameters have been calculated from similarly common kinetic models for adsorption phenomena.

Mixed metal isotherms observably are more difficult to model, due to heterogeneity, competition, saturation and desorption processes. A novel modified Langmuir model, which quantifies the desorption has been derived, which can predict experimental capacities of multiple species (though only in a defined system) relatively well.

Both the carboxylic acid-functionalised C107E resin and the iminodiacetic acid MTS9301 displayed high selectivity for copper, with C107E also adsorbing lead over iron(II) and zinc. MTS9301 displayed similar equilibrium uptake of all metals to single metal isotherm counterpart experiments, prior to saturation, apart from capacities being naturally reduced.

Kinetically, the uptake of copper, iron(II) and zinc was retarded for both C107E and MTS9301, with lead not displaying the same level of hindrance. Zinc and iron(II) were seemingly poorly competitive for binding sites for both resins, with copper and lead uptake not reaching saturation point, however, the higher-affinity metals exhibited a two-stage adsorption profile, which is proposed to reflect proton-metal exchange becoming metal-metal exchange. MTS9301 also displayed high desorption of lead, iron(II) and zinc, in favour of further copper uptake. TP214 displayed slower copper adsorption kinetics and a lower copper capacity than MTS9301, thereby decreasing the interest in this resin, in relation to this study.

C107E displayed the largest separation of iron(II), removal of which is not required to detoxify sewage sludge, from the three more hazardous metals. It had high capacities for each metal, but relatively slow kinetics. This would be useful for a system with heavy copper and lead contamination, but would be ineffective for zinc removal. As a single-step extractant, MTS9301 was the best performer overall. While its capacity for lead and zinc may be hindered via saturation with copper, with an appropriate resin to pulp ratio, this material would be an effective adsorbent. Considering the large concentration of iron within sewage sludge, and the possibility to avoid unnecessary adsorption of iron via kinetic separation, MTS9301 appears to be the optimal resin for the intended RIP system.

Credit author statement

James P. Bezzina: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Project administration, Thomas J. Robshaw: Data curation; Writing - original draft; Writing - review & editing, Adam J. Canner: Writing - review & editing, Robert Dawson: Funding acquisition; Supervision, Mark D. Ogden: Funding acquisition; Project administration; Supervision; Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2022.116279>.

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